

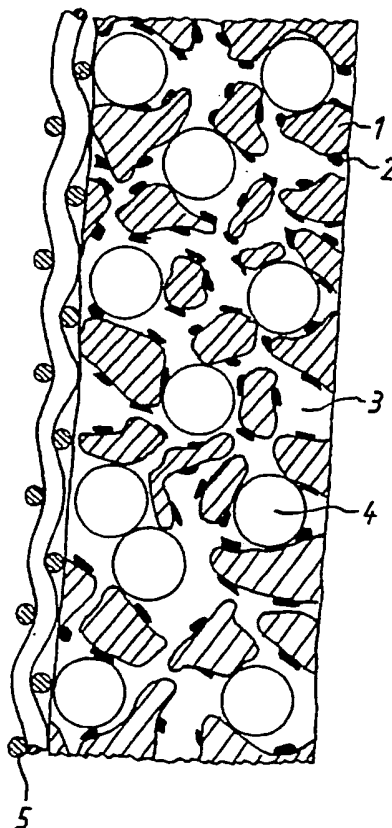
(12) UK Patent Application (19) GB (11) 2 013 102

A

- (21) Application No 7827785
- (22) Date of filing 23 Jun 1978
- (23) Claims filed 23 Jun 1978
- (30) Priority data
- (31) 2804154
- (32) 31 Jan 1978
- (33) Fed Rep of Germany (DE)
- (43) Application published  
8 Aug 1979
- (51) INT CL<sup>a</sup>  
B01D 39/16 53/02
- (52) Domestic classification  
B1T 1105 1401 1406  
1413 1419 1421 1422 1602  
1704 1705 1709 1811 1901  
AC  
B1L 102 DB
- (56) Documents cited  
GB 1476317  
GB 1377277  
GB 1368982  
GB 1203725  
GB 1169523  
GB 1125465
- (58) Field of search  
B1L  
B1T
- (71) Applicants  
Hubert von Blücher,  
Sohnstrasse 56, 4000  
Düsseldorf 1, Federal  
Republic of Germany and  
Hasso von Blücher,  
Sohnstrasse 56, 4000  
Düsseldorf 1, Federal  
Republic of Germany
- (72) Inventors  
Hubert von Blücher  
Hasso von Blücher
- (74) Agents  
Gee & Co.

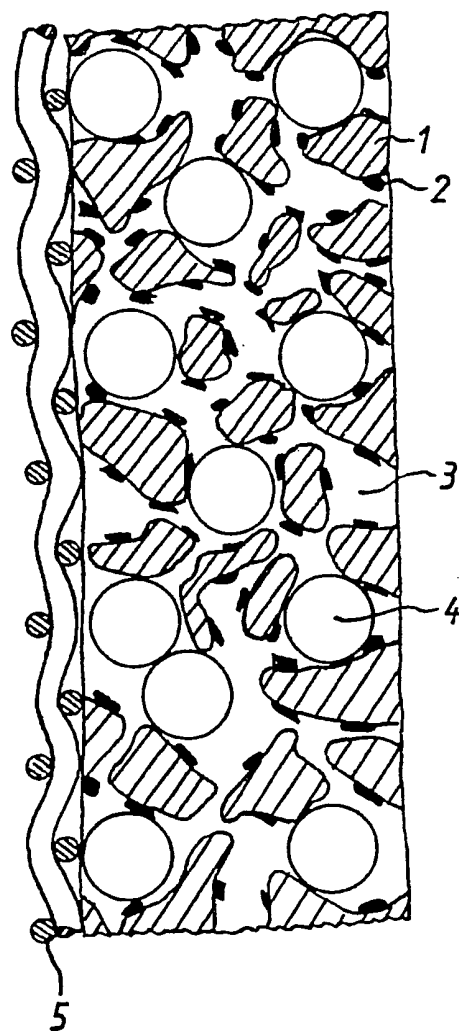
(53) A filter material and its manufacture

(57) A filter material, for example for use in the construction of safety clothing, gas masks or the like is made of an open-pored foam polyurethane (1) with adsorber particles (2) adhered to the pore walls and porous adsorber grains (4) placed in the pores. In a process for making the material the adsorber grains are forced into the foam, which is wetted with water, by means of an air current. The foam may be reinforced by means of a fibre layer (5) to prevent distortion of the pores and possible escape of the adsorber grains therefrom. The adsorber is preferably active carbon made by carbonizing coagulated viscose drops. The material is stated to prevent passage of liquid droplets as well as vapours.



GB 2 013 102

2013102



## SPECIFICATION

**A filter material and a method and apparatus for making it**

This invention relates to a filter material comprising an open-pored, flexible foam material base and adsorber particles supported by its pore walls, and to a method and an apparatus for making such a filter material.

In the design and making of safety apparatus, safety or protective clothing for human use and for medical apparatus, air-conditioning, water-processing and aircraft design there is a need for flexible filters for inhibiting the passage of vapours and gases which have a poisoning or otherwise damaging effect.

A known filter material of this sort (see German Specification No. 2,400,827) has the useful property that it is to some extent permeable to gases.

If however it is desirable to inhibit the passage of damaging materials in a liquid phase in addition to damaging materials in the form of gas or vapour, it has so far been necessary to employ a heavy duty filter in front of the gas or vapour filter, for the absorption of liquid materials, and this reduces the desirable properties of flexible sheet material such as a low weight, flexibility, low heat insulation and high air permeability.

In particular in safety apparatus as used in very rough conditions, as for example in fires, or for prevention of damage to persons or property in chemical plant, it has so far been necessary to use different sorts of apparatus each made for use in relation to one sort of damaging material. Light safety clothing, designed to permit operations in a thick mist of damaging material, can only be made of the initially mentioned, known filter material to a limited extent, since liquid damaging material readily permeates this filter material.

It is accordingly an object of the present invention to provide a filter material of the kind initially referred to that it is better at separating out damaging liquid substances without a decreased separating effect for vapours and gases, even when the filter material is completely wetted or a substantial movement of air is possible therethrough.

The present invention provides a filter material comprising an open-pored base of flexible foam material, said material incorporating adsorber particles supported upon its pore walls and porous adsorber grains located within its pores. The said adsorber grains in the pores do not impede the movement of gas through the pores to any important degree, while on the other hand, because of their porosity liquid is absorbed thereby and damaging substances are adsorbed. Even if generally all adsorber grains have taken up liquid to their maximum extent, the resistance to movement of gases through the filter material of the invention is not increased to any important extent.

Thus it is possible to make flexible air or gas filters which are able not only to take up a very great amount of liquids, but also to act as a liquid filter, because the effect of the porous adsorber grains

generally is to keep liquid elements in the material longer. Furthermore the filter material of the invention is in a position to absorb and retain within it large amounts of damaging liquid material without the material passing right through the filter.

If damaging liquid material is converted into a vapour form in the adsorber grains, the vapour will be adsorbed by the adsorber particles on the pore walls.

Thus the filter material of the invention makes possible on the one hand a high degree of ventilation and on the other hand the exclusion of skin and respiratory poisons and corrosive gases and liquids, by a sieve or filter action and surface forces. It may also act in a manner such as to make these materials safe chemically.

The air and/or liquid moving past the adsorber grains is rolled by the foam-specific arrangement of the pore systems of the foam material base from one pore layer into the next, lower one, and is thus forced past a large number of adsorber particles and adsorber grains, which have the effect of sedimentation sieves or filters and of separating damaging materials or substances from the air and/or liquid.

It is generally possible to arrange the size of the adsorber grains such that in each of the pores containing them more than one grain is arranged; however in order to make certain that base adsorber grains are not able to pass via the connection channels between separate pores of the foam material from one pore into the next, in one embodiment of the invention the adsorber grains are so sized that they generally take up the whole of the space in the full-size pores (that is to say the pores of the greatest size) in the foam material base. If the filter material is to be subject to a particularly large amount of damaging liquid material, and a design is needed in which the foam material base is thin or the air permeability of the filter material is not very important, it is generally possible to have adsorber grains in virtually all pores of the foam material base; in some cases it is advantageous to use a foam material base which has a large number of micro-pores and thus ensures a good air permeability so that all full-size pores may be filled by adsorber grains without decreasing the ventilation effect to a large extent. In a further development of the invention it is however advantageous if only 20 to 50% of the full-size pores of the foam material have the adsorber grains in them, so that about every second to every fifth pore has such an adsorber grain in it, the large number of pore layers and the irregular distribution of the adsorber grains enabling a high degree of filtering without the movement of air being substantially impeded.

It is generally possible to have adsorber grains with edges, such as octahedra, tetrahedra, cubes or six-sided blocks. In this respect the adsorber grains can have their edges touching the pore walls so that between their flat walls and the curved pore surface ventilation channels are present in all cases; however in further developments of the invention the use of grain forms without edges or with only a few edges, as for example ellipsoids or cylinders, is advantageous, since such grains are generally

speaking more readily placed in the pores of the foam material base. In this respect, in a further development of the invention, it is particularly advantageous if the adsorber grains have generally the same geometrical form as the pores, though they are smaller in size, so that in each pore a ventilation channel is at all times formed between the face of the adsorber grain and the wall face of the pore and, in a further form of the invention, use is more particularly made of spherical adsorber grains, which not only have the advantages noted earlier of edge-free grains but in addition are able to be made simply and at a low price with a high accuracy and with quite the right grain size needed so that the use of the filter material of the invention for normal purposes is advantageous not only for technical but also for price reasons.

Generally speaking it is possible to make use of foam material bases with any desired pore size and to correlate the size of the adsorber grains accordingly; in one development of the invention use is however made more particularly of adsorber grains with a diameter of about 0.01 to 0.001 mm and pore sizes as needed for such grains, since in the case of such a size a specially good air permeability and filter effect is achieved.

As a material for the adsorber grain it is possible to make use, for example, of kieselguhr, which in some cases has the necessary grain form in its natural form; however in order to make certain of a specially good filtering effect it is particularly useful for the adsorber grains to be made of active carbon and for the adsorber particles, present on the pore walls, to be formed by active carbon.

In the case of low air speeds and stationary use of the filter material it is generally likely that the adsorber grains will remain in the pores once they have been put in them; however in order to make possible use of the filter material of the invention in moving and shaking structures, and in the case of high air speeds the adsorber grains may be caused to adhere to the walls of the pores in which they are placed so that the distribution of the adsorber grains among the pores of the foam material base is substantially constant even in very rough conditions of use.

Although any foam material with the necessary mechanical properties and resistant to chemical attack is generally suitable as a foam material base for the filter material of the invention polyurethane foam material is preferably used, since this not only has all necessary mechanical and chemical properties, but furthermore is able to be made with pore sizes and pore distributions which are particularly advantageous. Furthermore this foam material allows the adhesion of the adsorber grains by means of heat processing.

In order to prevent excess stretching of the filter material in use such as would cause deformation of its pore shape and size with consequent displacement even of adhesively attached adsorber grains, the foam material base preferably has at least one fibre layer, made for example of fibres placed in position during foaming, so that the foam material base is not able to be stretched to such a degree that any

change in its filtering properties takes place.

Such a fibre layer is preferably in the form of a flexible grid running across the main direction of movement of material to be filtered. The grid is able to counteract any stretching in nearly all directions of the grid plane because of the crossing-over of separate fibres, and in this respect it is particularly advantageous if the grid is so made that its effective mesh size prevents the passage of the adsorber grains. The result is then that the adsorber grains are additionally fixed in position in certain zones of the foam material base because of the placing in it of grid layers, and they are kept in place even when the filter material is heavily loaded. In this respect a particularly good effect is made possible if the fibre layer is placed on at least one of the faces of the foam material base in order to make certain that even in the case of heavily loaded filters substantially no adsorber grains can be displaced from the foam material base, such as would change the filtering characteristics if it occurred.

If only one fibre layer is used, the layer is preferably on the outlet face of the filter in order to ensure that no adsorber grains are drawn from the support body by the current of filtered material. This is of particular importance in the case of breathing masks, because, unlike active carbon dust which does not have a damaging effect, trouble from adsorber grains is likely if they get into the eyes or parts of the breathing system.

Advantageously the fibre layer is formed of woven polyamide fibres because such fibres are not only chemically resistant and are mechanically strong, but they are also particularly well able to retain the adsorber grains in the foam layer base.

The loose, woven polyamide fibre structure is more particularly bonded, welded, or fixed by adhesives on the face of the foam material base.

The filter material of the invention is not only better at absorbing and filtering liquids than known material, but furthermore – and this is very surprising – has a very much better effect on filtering vapours and gases because of the additional active faces provided by the adsorber grains.

The filter material of the invention might be made by mixing the adsorber grains in with the components of the foam material base before it is caused to foam, although a complete wetting of the adsorber grains must be prevented.

Alternatively, a layer of adsorber grains might be placed over a surface of the dry foam material base and then violently vibrated, for example by a sound generating apparatus, so that the adsorber grains are introduced into the foam material base.

However, the most even distribution of the adsorber grains in the foam material base is achieved in an embodiment of the invention in which the adsorber grains are forced into the aqueous-wet foam material base by means of an air current. Because air is readily able to pass through the foam material base, a substantial part of the air current will in fact pass through the foam material base and, in so doing, will ensure that the adsorber grains are admitted to the inside of the foam material base. When adsorber grains issue from the rear of

the foam material base the degree to which the base has taken up adsorber grains can be determined. Preferably the foam material base has the adsorber particles arranged on its pore walls prior to the step of introducing the adsorber grains, and in particular use may be made of a polyurethane foam base with active carbon particles welded on its pore walls. It is possible to make the polyurethane foam so hard or so yielding that on subsequent blowing or forcing of the adsorber grains into it the grains penetrate the base to the desired degree. The liquid wetting the foam material base has the effect of a lubricant.

As noted it is possible to see from the degree to which the adsorber grains issue from the foam material base into which they are forced, how far its pores have taken up adsorber grains. However once the blowing time has been experimentally determined for a certain thickness of the foam material base and at a certain air current speed it will not be necessary to make further observations during an actual production process. In production, it is therefore advantageous, in order to ensure that there is no damage to the complete filter material, to use a foam material base which on its face turned away from the blowing air current is coated with fibre fabric, more particularly polyamide fibre woven fabric, which as noted earlier both strengthens the filter material and prevents any undesired distortion of the foam material base, thus helping to ensure that the base takes up the adsorber grains evenly.

For making the adsorber grains it seems to be possible to make use of a granular material with a suitable grain form and size, such as diatoms taken from kieselguhr, and to put, if necessary, active carbon particles in the porous hollow spaces of these grains.

In a particularly advantageous embodiment of the invention however the adsorber grains are made synthetically from active carbon by putting viscose droplets in a Lewis acid and then subjecting them to a carbonization process while being continuously drummed or tumbled. On placing the droplets in the acid the latter permeates the viscous material; the viscose bodies, still wet, are then placed in a centrifuge and made to go through a carbonization process while being continuously drummed or tumbled to produce spherical adsorber grains with the best specific surface area and which acquire a hard-porous surface in the drumming or tumbling operation, while on the other hand inside they have a porous sponge-like structure. The hard outer face makes the adsorber grains very strong and makes possible the blowing of the grains into the foam material base without the grains being broken by abrasion, by impact, or because they escape from the pore openings.

It is generally possible to place the foam material base, after the particles have been blown into it, in a weak solvent, which renders the faces of the pore walls soft so that the adsorber grains on the pore walls are caused to stick to them.

However in order to render unnecessary the immersion in a solvent and subsequent repeated washing of the foam material base for washing of the adsorber grains, in one embodiment of the

invention the foam material base with the blown-in particles is subjected to a temperature of 160°C to 190°C for thermofixing of the adsorber grains on the lamellae of the foam pores, the adsorber grains which are more particularly ball-shaped, being joined at the points of contact with the foam material base sufficiently strongly that they have a free face which is not changed in any way so that their effect is generally not decreased by adhesion to the pore walls.

To make blowing in of adsorber grains into the foam material base possible the pore openings have to yield to a certain degree to admit the adsorber grains. Thus preferably the foam material base is vulcanised after the above-mentioned heat treatment for about 6 hours at 120°C in order, on the one hand, to provide the desired characteristic for the filter material produced, and, on the other hand, to reduce yielding of the pore openings so that the grains are retained in their pores.

Viscose drops for the adsorber grains might be produced by placing thick viscose on a rotating disc, from which drops of different sizes are forced off by the centrifugal effect and after the above-mentioned drumming or tumbling of the active carbon grains, the grains may be grouped in different sizes, for example using an air classifying apparatus. In order to reduce the waste which otherwise takes place with such a method, however, in a further embodiment of the method of the invention for producing viscose drops of even size, the viscose is extruded in an extruder by a series of consecutive pressure impulses, more particularly using highly compressed air, and the nozzles of the extruder are oscillated to ensure that the drops are broken off. An extruder as used for example for making artificial silk is very good for this purpose if at its lower end there are arranged a number (500 and more) of small nozzles; by heating viscose in a liquid form using consecutive impulses, high compressed air is forced into the melting zone of the extruder and through the nozzles in small amounts. By electro-magnetically produced vibration of the nozzle groups these small amounts are broken off from the nozzle ends as drops and then they are able simply to fall into an acid vessel placed under the extruder. Drops of even size are produced, with a grain size of 0.01 to 0.001 mm.

For producing bodies of nearly complete spherical form of synthetic active carbon from the drop-like viscose bodies after drumming or tumbling and which have a specific surface area of approximately 1200 m<sup>2</sup>/g (N : BET), the drops may be processed for approximately 10 minutes in the Lewis acid till they have taken up to 10% of the acid.

The Lewis acid used is preferably aluminium chloride or barium chloride, which have been noted to be particularly advantageous.

It is possible for the viscose bodies taken out of the Lewis acid firstly to be dried and then drummed or tumbled so that any uneven parts are rubbed off. However, advantageously the viscose bodies taken out of the Lewis acid are drummed or tumbled while still wet and to a certain extent plastically deformable, since in this case it is not only possible to be certain of the desired spherical grain form without a

very large amount of material being rubbed off, but additionally the grain face is made denser so that the outer face of the individual adsorber grains is much harder than normal and is not damaged by abrasion, while the inner walls and the inner part of the spherical grains is still porous and soft and for this reason has very good absorption properties.

During drumming, the viscose bodies are preferably heated to 600°C to 900°C in the absence of air for carbonizing and are then treated for 15 to 60 minutes with water-vapour; this treatment time, which is comparatively short, makes for a violent movement and thorough and continuous mixing of the viscose bodies, which is needed for a complete, even carbonization and activation of the grains.

In place of water-vapour it is possible to use  $\text{CO}_2$ ,  $\text{AlCl}_3$  or  $\text{BF}_3$ , enabling a processing time of only 15 to 60 minutes, dependent on the design of the plant.

It is furthermore to be noted that the product made is cleaner and more free of dirt if more gas or vapour is forced through the carbonization zone when carbonization is taking place.

For ensuring a particularly even, spherical grain form there may be used for making the adsorber grains a drum apparatus in accordance with the invention, which has a concave rotary centrifuge cylinder capable of being shut, a lower plate turning in the opposite direction and forming the lower end of the cylinder, a part near the inner wall of the centrifuge cylinder, more particularly made of razor-blade steel, for changing the direction of the material, and inlet and outlet connections for carbonizing and activating gas or vapour. Once they have been put in the drum apparatus turning over of the viscose bodies is caused by the centrifuge cylinder and they are forced against the direction changing part, which deflects them clear of the rotating cylinder wall and they are forced against the lower plate turning in the opposite direction. From this position they are then again forced against the cylinder wall and then come back on to the lower plate again.

For causing this process to take place approximately 1500 times per minute, one form of the drum apparatus of the invention is so designed that the lower plate and the centrifuge cylinder are designed to turn in opposite directions, each at a speed of about 1500 rpm.

Samples of a filter material in accordance with the invention were tested in relation to samples of normal sheet filter material, each having a surface size of 4 cm<sup>2</sup>, by dropping dichlorodiethyl sulphide thereon.

After 6 hours the amount of this chemical which had penetrated the filter per cm<sup>2</sup> was measured.

#### Outcome of tests

Filter material of the invention Two layers (in micrograms)

(a) 0.35 0.37 penetrated per 1 cm<sup>2</sup>

(b) 0.25 0.27 penetrated per 1 cm<sup>2</sup>

Filter material of the invention Three layers

(a) 0.60 0.62 penetrated per 1 cm<sup>2</sup>

(b) 0.57 0.45 penetrated per 1 cm<sup>2</sup>

Normal sheet filter material

(a) 2.52 2.42 penetrated per 1 cm<sup>2</sup>

(b) 2.05 2.00 penetrated per 1 cm<sup>2</sup>

The acceptable tolerance limit for filter materials is 4 micrograms/cm<sup>2</sup>. Thus the normal sheet filter only reaches half of the limit for material penetrating the filter, while the material of the invention having spherical adsorbers of synthetic active carbon only reaches a tenth of this.

An account in more detail of one form of the invention is now given referring to the accompanying diagrammatic drawing, not to scale, the single figure of which is a section through a filter material in accordance with the invention.

Referring to the drawing, sheet material 1 of polyurethane foam material is bonded at one face with knitted material 5 of polyamide filaments, so that a filter material is made with a thickness of approximately 2 mm.

Directly on the pore walls of the foam material base 1 active carbon particles 2 are fixed by adhesion. They are responsible for cleaning air going through the filter material in the direction of the arrow and freeing it of poisons.

A proportion of the full-size pores 3, that is to say the pores of greatest size, of the foam material base have adsorber grains 4 therein, that is to say one grain in each pore. The grain takes up more or less the whole of the full-size pore 3 and it is fixed to the pore wall by bonding or adhesion.

The covering 5 of woven material has its mesh of such a size that it is smaller than the diameter of an adsorber grain 4 and as a result the adsorber grains 4 are not able to escape from the foam material base 1 in the direction of the arrow.

In addition to viscose it is possible to use polyamides, polyesters or polyethylene as an extrudate for making the adsorber grains.

#### CLAIMS

1. A filter material comprising an open-pored base of flexible foam material, said material incorporating adsorber particles supported upon its pore walls and porous adsorber grains located within its pores.

2. A filter material as claimed in Claim 1, in which the said adsorber grains are located in the full-sized pores of the foam material and are of such a size that they each take up substantially the whole of the volume of the respective pore of the foam material base.

3. A filter material as claimed in Claim 1 or Claim 2, in which 20% to 50% of the full-size pores of the foam material base have adsorber grains in them.

4. A filter material as claimed in any one of Claims 1-3, in which the adsorber grains have a shape similar to that of the pores.

5. A filter material as claimed in Claim 4, in which the adsorber grains are of spherical form.

6. A filter material as claimed in any one of Claims 1-5, in which the adsorber grains have a diameter of 0.01 to 0.001 mm.

7. A filter material as claimed in any one of Claims 1-6, in which the adsorber grains are made of active carbon.

8. A filter as claimed in any one of Claims 1-7, in which the adsorber grains adhere to the pore walls.

9. A filter material as claimed in any one of

Claims 1-8, in which the foam material base is made of polyurethane foam material.

10. A filter material as claimed in any one of Claims 1-9, in which the foam material base has at least one fibre layer.

11. A filter material as claimed in Claim 10, in which the fibre layer is a flexible grid arranged transverse to the direction of flow of a medium to be filtered and its effective mesh size is less than the dimension of the adsorber grains.

12. A filter material as claimed in Claim 10 or Claim 11, in which the fibre layer is arranged on at least one of the faces of the foam material base.

13. A filter material as claimed in Claims 12, in which the fibre layer is arranged on the outlet face of the foam material base.

14. A filter material as claimed in any one of Claims 11-13, in which the fibre layer is made of woven polyamide fibres, and this material is welded or adhesively fixed on a face of the foam material base.

15. A filter material substantially as described herein with reference to the accompanying drawing.

16. A method for making a filter material as claimed in any one of Claims 1-15, wherein the said foam material base, upon the pore walls of which active carbon particles have been attached, is wetted with water and is placed in the path of an air current containing adsorber grains whereby the latter are forced into the foam material base under the influence of said air current.

17. A method as claimed in Claim 16, wherein the said adsorber grains are prepared by placing viscose drops in a Lewis acid and then carbonizing said drops during a continuous drumming or tumbling process.

18. A method as claimed in Claim 16 or Claim 17, in which the foam material base into which the grains have been forced is heat-treated at a temperature of 160 to 190°C.

19. A method as claimed in Claim 18, in which after said heat-treatment the foam material base is vulcanized for about 6 hours at 120°C.

20. A method as claimed in any one of Claims 17-19, in which the said viscose drops are prepared by extruding viscose from an extruder by means of consecutive pressure impulses of highly compressed air and by oscillation of the extruder nozzles so that the drops are broken off.

21. A method as claimed in any one of Claims 17-20, in which the said drops are immersed in the Lewis acid for about 10 minutes.

22. A method as claimed in any one of Claims 17-21, in which the said Lewis acid is aluminium chloride or barium chloride.

23. A method as claimed in any one of Claims 17-22, in which the viscose bodies, after removal from the Lewis acid are drummed or tumbled while still wet.

24. A method as claimed in any one of Claims 17-23, in which the viscose bodies during drumming or tumbling are heated to 600 to 900°C in the absence of air and are then treated with water-vapour for 15 to 60 minutes, in order to effect carbonization and activation thereof.

25. A method as claimed in any one of Claims 17-23, in which the viscose bodies during drumming or tumbling are heated to 600 to 900°C in the absence of air and are then treated with  $\text{CO}_2\text{AlCl}_3$  or  $\text{BF}_3$  for 15 to 60 minutes, in order to effect carbonization and activation thereof.

26. A method for making filter material as claimed in any one of Claims 1-15, substantially as described herein.

27. A drum apparatus for carrying out the method as claimed in any one of Claims 17-26, comprising a closable rotary centrifuge cylinder of concave shape, a plate bounding the cylinder at the lower end and arranged to rotate in the opposite direction from the cylinder, a direction changing member arranged adjacent the inner wall of the centrifuge cylinder and inlet and outlet connections for carbonizing and activating gas or vapour.

28. A drum apparatus as claimed in Claim 27, in which the bottom plate and the centrifuge cylinder are designed to rotate in opposite directions at about 1500 rpm in each case.

29. The features herein described, or their equivalents, in any novel selection.

Printed for Her Majesty's Stationery Office by The Tweeddale Press Ltd., Berwick-upon-Tweed, 1979.  
Published at the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.